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SELF-DIFFUSION OF MACROMOLECULES IN POLYSTYRENE SOLUTIONS*

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Pulse NMR has been used to study the self-diffusion of the macromolecules of fractionated PS in solutions of CCl_4 and C_6D_6 over wide concentration and temperature ranges, revealing the existence of a spectrum of values of the coefficients of self-diffusion D due to the fluctuations in the entanglements between the macromolecules. The mean weighted D is an objective characteristic of the translationar mobility of the macromolecules in the systems studied. The concentration, molecular-mass and temperature relations of mean weighted D are discussed in relation to existing theories.

A FUNDAMENTAL value characterizing the translational mobility of the macromolecules in melts and solutions is the self-diffusion coefficient D. One of the direct methods of measuring it is pulse NMR with a pulse gradient of the magnetic field. In the present work this method is used to measure D of the macromolecules of fractionated PS over wide concentration and temperature ranges and to analyse the special features of measurement of D in polymer solutions and the regularities obtained.

We used solutions of PS fractions with $M_w/M_n < 1{\cdot}2$ and with number average MM $0{\cdot}24\times10^6$, $0{\cdot}38\times10^6$ and $1{\cdot}36\times10^6$ in completely deuterized benzene C_6D_6 of the Izotope Association and carbon tetrachloride CCl_4 of pure for analysis grade. The content of PS in the solutions (its concentration c) varied from 1·7 to 480 kg per m^3 of solutions. Temperature range 30–70°C. The notations and some characteristics of the samples are given in the Table. D for the macromolecules was measured by the stimulated echo technique [1] at the frequency of proton resonance 60 MHz with a pulse gradient g of the magnetic field the maximum value of which was 30 T/m [2]. The diffusion time t_d varied from 10 to 400 msec. To raise the signal-to-noise ratio we used digital accumulation of the echo signal.

Form of diffusion decay. It is known that if the sample is characterized by a single D then the decay of the amplitude of the spin echo signal depending on the amplitude of the pulse gradient g (diffusion decay $A(g^2)$ is described by the relation [3]

$$A(g^2)=A(0)\exp(-\gamma^2\delta^2g^2Dt_d), \quad (1)$$

where $A(0)$ is the amplitude of the echo signal for a pulse gradient of the magnetic field $g=0$; δ is the duration of the gradient pulses; γ is the gyromagnetic ratio for the proton. In the solutions studied for all PS fractions at $c<20$ kg/m^3 the observed diffusion decay is described by the expression (1)

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